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The Ternary System Titanium–Aluminum–Nitrogen*

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The phase equilibria in the ternary system titanium–aluminum–nitrogen are investigated for two isothermal sections. At 1273 K one encounters the H-phase Ti_2AlN (a = 0.29912 nm, c = 1.3621 nm) and the cubic perovskite-type phase Ti_3AlN (a = 0.41120 nm). At 1573 K one encounters additionally $Ti_3Al_2N_2$ (space group: $P31c$, hexagonal axes a = 0.29875 nm, c = 2.3350 nm). α-Titanium dissolves nitrogen and aluminum to a large extent, but no solubility of the third element was detected in any of the other binary phases.

Introduction

Reports on the outstanding hardness and abrasive properties of the ternary nitride Ti_2AlN (*1*), as well as cermets based on AlN–Ti (*2*), have generated interest in the constitution of the ternary system: titanium–aluminum–nitrogen.

Only limited information is found in the literature on this ternary system: The $\alpha \rightleftharpoons \beta$ transformation in titanium with increasing aluminum and nitrogen concentration was investigated by Van Thyne *et al.* (*3*), and the H-phase Ti_2AlN (a = 0.2994 nm, c = 1.361 nm) was studied by Jeitschko *et al.* (*4*) and was recently confirmed (*5*).

Above 1000 K, the diagram of titanium–aluminum, as presented in the just-published compilation by Kubaschewski-von Goldbeck (*6*), consists of the five intermediate phases $TiAl_3$, Ti_2Al_5 (or Ti_5Al_{11}), $TiAl_2$, TiAl, Ti_3Al, and exhibits wide ranges of solid solutions of α-Ti and β-Ti. This compilation does not include the results of the redetermination of the α-Ti and Ti_3Al phase boundaries by Swartzendruber *et al.* (*7*) which agree remarkably well. At temperatures below 1000 K, $TiAl_3$ transforms into the ordered modifications Ti_9Al_{23} (*8*) or Ti_8Al_{24} (*9*) and $Ti_{16}Al_{48}$ (*10*).

The phase diagram of titanium–nitrogen system was updated recently by Bars *et al.* (*11*). The nitrogen-rich boundary of α-Ti(s.s) was accurately determined; ε-Ti_2N was found to exist at least up to 2273 K. The structure of the low temperature modi-

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fication of Ti_2N, which was first described by Lobier *et al.* (*12*), was confirmed by electron diffraction (*13*) and by neutron diffraction (*14*). This phase was found to exist up to 1073 K, while between 1173 and 1273 K a two-phase region ε-Ti_2N + TiN_{1-x} was observed for the composition $TiN_{0.49}$ (*14*).

Aluminum nitride is the only reported compound in the binary aluminum–nitrogen system (*15*).

Experimental

Binary Ti–Al master alloys were prepared by arc melting mixtures of aluminum powder (2N8, containing Fe 0.1%, Si 0.05%, other 0.02%; from Alpha Div., Ventron Corp.) and titanium powder (2N, containing Ca 0.4%, Al 0.35%, Fe 0.1%, C 0.015%, Si 0.003%, Sn 0.002%, other 0.003%; from Alpha Div., Ventron Corp.). These master alloys were pulverized and mixed with AlN powder (2N, a = 0.31080 nm, c = 0.49662 nm, Alpha Ventron GmbH., FRG), TiN powder (2N, a = 0.4243 nm, Alpha Div., Ventron Corp.) and Ti-powder. About 30 ternary alloys were cold-pressed and sintered: (a) at 1273 K for 240–800 h in BN crucibles, sealed in evacuated quartz tubes; (b) at 1473 K for 60 h in Mo crucibles under dynamic vacuum (10^{-4} Pa); (c) at 1573 K for 60 h in Mo crucibles under dynamic vacuum (10^{-4} Pa); (d) at 1573 K for 50 h in BN crucibles under argon ($1{,}013 \times 10^5$ Pa); (e) at 1573 K for 50 h in Mo crucibles under argon ($1{,}013 \times 10^5$ Pa); (f) at 1673 K for 30 h in Mo crucibles under dynamic vacuum (10^{-4} Pa).

The alloys sintered at 1273 K were initially not in equilibrium. These alloys were pulverized again, cold-pressed, and sintered. Alloys sintered under dynamic vacuum at 1673 K showed loss of aluminum; neither the variation of the external nitrogen partial pressure over a wide range nor the use of different crucible material, especially nitride material, significantly affected the phase equilibria at the temperatures investigated here. The sintered alloys were analyzed by X-ray diffraction, and by optical and electron microscopy.

The choice of powders as starting materials increases the oxygen impurity level of the specimen due to the oxide layer surrounding each powder particle. However, no oxide or oxynitride phases have been observed. The lattice parameters found for binary or ternary phases of the Ti–Al–N system closely match those reported in the literature (as given in Refs. (*4*, *6*, *15*)). This indicates that the amount of impurity introduced by this preparation method affects the investigated phase equilibria only to such a small degree, that this remains within the other experimental uncertainties of investigations in ceramic multicomponent systems. A possibly notable exception is the α-Ti(s.s.) + β-Ti(s.s.) phase field as discussed in the next section.

Experimental Results and Discussion

Phase Equilibria at 1273 K

At 1273 K there exists a ternary phase with the approximate composition Ti_3AlN and the H-phase Ti_2AlN. This new Ti_3AlN phase has a cubic structure with a lattice parameter of a = 0.41120 nm, which varies only within experimental errors, indicating a negligible homogeneity range of that phase. A comparison between calculated and observed X-ray diffraction intensities (Table 1) shows that Ti_3AlN is isotypic with Ti_3AlC (*16*). At 1273 K Ti_3AlN coexist with TiN_{1-x}, Ti_3Al, and Ti_2AlN.

The lattice parameters observed for Ti_2AlN are a = 0.29912 and c = 1.3621 nm, in agreement with Jeitschko *et al.* (*4*). Ti_2AlN was found to coexist at 1273 K with Ti_3AlN, TiN_{1-x}, AlN, TiAl, and Ti_3AlN.

AlN does not dissolve detectable amounts of titanium, as detected by lattice parameter measurements. The lattice pa-

TABLE I

X-RAY POWDER DIFFRACTOGRAM OF Ti_3AlN ($CuK\alpha$-RADIATION)

hkl	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
100	.0354	.0351	m	19
110	—	.0703	—	0
111	.1055	.1054	vs	100
200	.1408	.1406	s	65
210	.1760	.1757	vw	5
211	—	.2109	—	0
220	.2814	.2812	m	38
221	—	.3163	—	2
300				0
310	—	.3515	—	0
311	.3865	.3866	m	33
222	.4220	.4218	w	12
320	—	.4569	—	1
321	—	.4921	—	0
400	.5624	.5624	vw	5
410	—	.5975	—	1
322				0
330	—	.6326	—	0
411				0
331	.6675	.6678	w	17
420	.7030	.7029	w	22
421	—	.7381	—	1
332	—	.7732	—	0
422	.8436	.8435	w	28
430	—	.8787	—	1
500				0
431	—	.9138	—	0
510				0
333	.9490	.9490	m	13
511				39

rameters of AlN in equilibrium with TiN_{1-x}, with Ti_2AlN, or TiAl do not deviate significantly from those for the binary compound (*15*).

TiN_{1-x} exhibits a wide range of homogeneity in the binary titanium–nitrogen system (*11*). However, the alloy TiN + 2 at% Al did not exhibit a single phase microstructure. TiN_{1-x} apparently parallels the solubility behavior of the analogous TiC_{1-x}–Al system, where microprobe analysis showed that aluminum is only marginally soluble in this phase (*17*); these data were taken over a range of carbon content in TiC_{1-x}. Similar results were obtained in the related system ZrN–Al (*18*). Therefore, it is assumed that the observed variation of the lattice parameter of TiN_{1-x} in ternary Ti–Al–N alloys reflects solely the difference in nitrogen content of that phase. Using Christensen's lattice parameter vs composition data as a basis (*19*) one can obtain the composition of the vertices [TiN_{1-x}, (TiN_{1-x} + αTi(s.s.) + Ti_3Al)], [TiN_{1-x}, (TiN_{1-x} + Ti_3Al + Ti_3AlN)], [TiN_{1-x} (TiN_{1-x} + Ti_3AlN + Ti_2AlN)], and [TiN_{1-x}, (TiN_{1-x} + Ti_2AlN + AlN)].

ε-Ti_2N was not observed to coexist either with one of the ternary phases or with one of the binary Ti–Al phases. It is concluded that phase fields containing ε-Ti_2N are confined to compositions close to the Ti–N binary by a tie line TiN_{1-x} + αTi(s.s.) (Fig. 1).

The lattice parameters of α-Ti(s.s.) in equilibrium with TiN_{1-x} and Ti_3Al are a = 0.29565 nm and c = 0.47564 nm. Limited data are available on the lattice parameter dependence of binary α-Ti(N,s.s.) vs nitrogen content (*11*) and α-Ti(Al,s.s.) vs Al content (*20, 21*). However, it seems doubtful whether a linear variation of the lattice parameters occurs within the phase field of

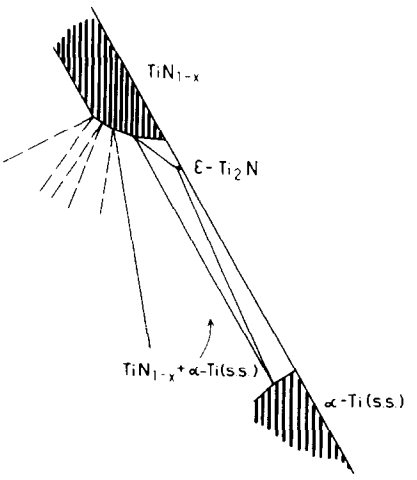

FIG. 1. Detail of the isothermal phase partition at 1273 K. The phase equilibria at compositions close to the binary Ti–N (schematic).

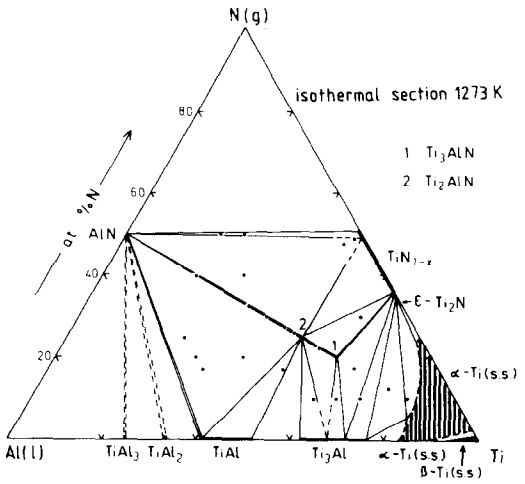

FIG. 2. Isothermal section at 1273 K. (Details close to ε-Ti_2N are omitted.)

α-Ti(Al + N,s.s.) such as, e.g., in Ni_3AlC_{1-x} (*22*). Rather a nonlinear dependence on composition like in the analogous Zr(Al + N,s.s.) (*23*) can be anticipated. Furthermore, titanium is an excellent getter material, and the lattice parameter of α-Ti(s.s.) might be affected by the oxygen impurity as starting materials. Because of this fact, the composition of the vertex [α-Ti(Al + N,s.s.), (α-Ti(Al + N,s.s.) + TiN_{1-x} + Ti_3Al)] is only derived from the relative amount of phases present in alloys containing α-Ti(s.s.) and their nominal composition.

Analogous considerations apply to the Ti_3Al phase. The compositions of the vertices of Ti_3Al containing three phase fields are only tentative, and more work is necessary, particularly, to examine the possible nitrogen solubility in this phase.

In specimens annealed in BN crucibles under argon a three-phase equilibrium TiN_{1-x} + Ti_3AlN + Ti_3Al is observed (e.g., in alloy $Ti_{0.65}Al_{0.175}N_{0.175}$, T = 1273 K). However, the phases Ti_3AlN and α-Ti(s.s.) coexist in alloys annealed in a Mo crucible under otherwise identical conditions.

The complete isothermal section at 1273 K is presented in Fig. 2. The investigated compositions are marked by points. The binary Ti–Al and Ti–N phase boundaries are taken from Refs. (*6, 7*) and (*11*), respectively. As no alloys were prepared containing more than 50 at% aluminum the phases $TiAl_2$ and $TiAl_3$ were not observed, but they are included in the diagram. However, ε-Ti_2N and the phase equilibria of this phase are not shown for clarity. Partially dashed tie lines indicate that the composition of the vertex is only estimated. The α-Ti(Al + N,s.s.) + β-Ti(Al + N,s.s.) phase field computed from Van Thyne's (*3*) data is shifted to higher (Al + N) concentrations as compared to the binary phase boundaries of the α-Ti(N,s.s.) + β-Ti(N,s.s.) and α-Ti(Al,s.s.) + β-Ti(Al,s.s.) phase fields given by Refs. (*6, 7*) and (*11*), respectively. This indicates that the phase boundaries in this section of the phase diagram are very sensitive to impurities (*11*); thus, additional data with high purity methods and materials are needed.

Phase Equilibria at 1573 K

In addition to Ti_2AlN and Ti_3AlN, which have the same lattice parameters as at 1273

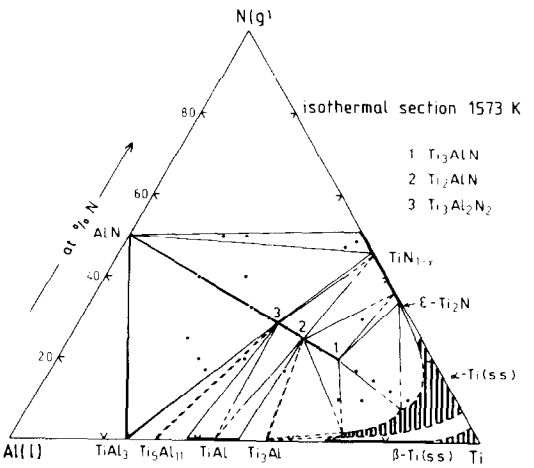

FIG. 3. Isothermal section at 1573 K. (Details close to ε-Ti_2N are omitted.)

TABLE II

X-RAY POWDER DIFFRACTOGRAM OF $Ti_3Al_2N_2$ (Cu$K\alpha$-RADIATION)

hkl	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
001	n.o.	.0011	n.o.	n.c.
002	n.o.	.0044	n.o.	n.c.
003	—	.0098	—	n.c.
004	.0176	.0175	m(16)	23
005	—	.0273	—	0
006	—	.0393	—	5
007	—	.0535	—	0
008	—	.0699	—	3
009	—	.0885	—	0
100	—	.0889	—	0
101	.0895	.0900	mw(20)	19
102	.0932	.0933	m(30)	56
103	—	.0987	—	2
104	.1057	.1064	ms(44)	77
00.10	.1090	.1092	ms(45)	58
105	.1167	.1162	s(83)	89
106	.1282	.1282	s(100)	100
00.11	—	.1321	—	0
107	.1426	.1424	m(24)	20
00.12	—	.1513	—	1
108	.1589	.1588	m(16)	15
109	.1773	.1774	m(17)	16
00.13	—	.1846	—	0
10.10	.1975	.1981	w(5)	3
00.14	—	.2140	—	0
10.11	.2206	.2210	m(30)	10
00.15	—	.2457	—	0
10.12	.2465	.2462	m(32)	7
110	.2667	.2667	ms(70)	70
111	—	.2678	—	0
112	.2734	.2711	w(13)	4
10.13		.2735		5
113	—	.2765	—	0
00.16	—	.2796	—	0
114	—	.2842	—	2
115	—	.2940	—	0
10.14	.3028	.3030	m(29)	20
116	—	.3060	—	1
00.17	—	.3156	—	0
117	—	.3202	—	0
10.15	.3346	.3346	mw(18)	15
118	—	.3366	—	0
00.18	—	.3538	—	0
119	—	.3552	—	0
200	—	.3556	—	0
201	—	.3567	—	2
202	—	.3600	—	6
203	—	.3655	—	0
10.16	.3680	.3685	m(30)	11
204		.3731		11
11.10	.3765	.3759	ms(51)	51
205	.3822	.3829	w(18)	11
00.19	—	.3942	—	0
206	.3944	.3949	m(22)	13
11.11	—	.3989	—	0
10.17	—	.4045	—	0
207	—	.4091	—	2
11.12	—	.4240	—	1
208	—	.4255	—	3
00.20	.4367	.4368	w(15)	9
10.18	—	.4427	—	3
209	—	.4441	—	3
11.13	—	.4513	—	0
20.10	—	.4648	—	1
11.14	—	.4808	—	0
00.21	—	.4816	—	0
10.19	—	.4831	—	1
20.11	.4874	.4878	w(6)	3
11.15	—	.5124	—	0
20.12	.5128	.5129	w(6)	3
10.10	—	.5257	—	0
00.22	—	.5285	—	0
20.13	.5399	.5402	vw	2
11.16	—	.5463	—	1
20.14	.5991	.5697	w(11)	10
10.21	—	.5705	—	1
00.23	—	.5777	—	0
11.17	—	.5823	—	0
20.15	.6006	.6013	w(12)	6
10.22	—	.6174	—	2
11.18	—	.6205	—	1
210	—	.6223	—	0
211	—	.6234	—	2

Note. s, Strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; n.o., not observed; n.c., not calculated.

K, a third ternary phase with the formula $Ti_3Al_2N_2$ exists at 1573 K. This phase is in equilibrium with TiN_{1-x}, AlN, $TiAl_3$, and Ti_2AlN (Fig. 3). The compound forms only within a narrow temperatre range, as it was not observed in specimens annealed at 1473 K, and had already decomposed at temperatures slightly above 1573 K.

$Ti_3Al_2N_2$ has a layered structure with a large lattice parameter in one direction. In analogy to the method of solving the struc-

TABLE III

CRYSTAL STRUCTURE DATA OF $Ti_3Al_2N_2$

Trigonal, space group $P31c$ (No. 159) Hexagonal axes a = 0.29875 nm, c = 2.3350 nm Atomic positions				
2	Ti in (2a)	0, 0, z;	0, 0, $\frac{1}{2} + z$	z = .35
1.8	Ti in (2b)	$\frac{1}{3}$, $\frac{2}{3}$, z;	$\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{2} + z$	z = .05
1.8	Ti in (2b)			z = .45
0.2	Ti in (2b)			z = .55
0.2	Ti in (2b)			z = .95
2	Al in (2a)			z = .15
2	Al in (2b)			z = .25
1.8	N in (2b)			z = .60
1.8	N in (2b)			z = .90
0.2	N in (2b)			z = .10
0.2	N in (2b)			z = .40

ture of $ZrAl_3C_{5-x}$ (*24*), the geometrical data of related compounds (e.g., AlN, Ti_2AlN, TiN_{1-x}) were analyzed in order to calculate the distance between each layer and the z-parameter of the atoms. Then the stacking sequence of the metal layers was determined to be ABABACBCBC by fitting of the powder intensity data (Table II). Further improved matching of observed and calculated intensities should be obtained by least-squares refinement of the nitrogen positions. The crystallographic data are given in Table III.

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